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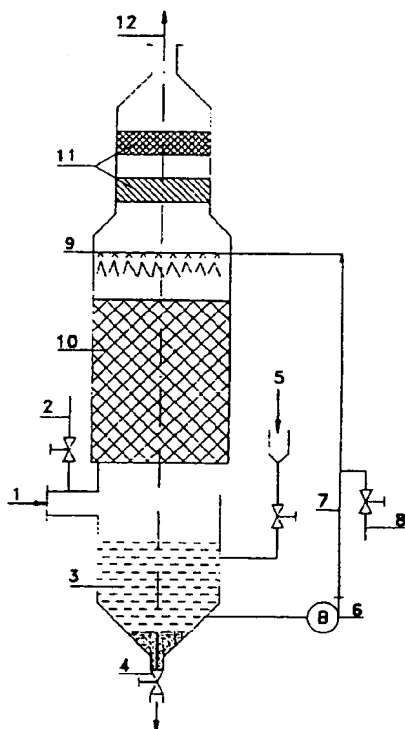
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(54) Titre : PROCEDE CONTINU POUR LA COLLECTE ET LA PRECIPITATION SIMULTANEE DU MERCURE DE
GAZ EN CONTENANT

(54) Title: CONTINUOUS PROCEDURE FOR THE SIMULTANEOUS COLLECTION AND PRECIPITATION OF
MERCURY IN GASES CONTAINING IT



(57) Abrégé/Abstract:

Procedure for the simultaneous collection and precipitation of mercury from mercury-containing gases. The procedure consists of passing the mercury gas through a washing tower where hydrogen sulphur (gas) is continuously and intermittently injected at the same time that it is watered with a solution containing a mercury complex (II) stable in semi acid, such as $[I_2Hg]^{2-}$ or $[(SCN)_4Hg]^{2-}$, without requiring the use of an additional oxidant. Both the collection and precipitation of the mercury and the regeneration of the solution containing the mercury complex (II) take place simultaneously in just one stage.

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ABSTRACT

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5 mercury-containing gases. The procedure consists of passing the mercury
gas through a washing tower where hydrogen sulphur (gas) is continuously
and intermittently injected at the same time that it is watered with a solution
containing a mercury complex (II) stable in semi acid, such as $[I_2Hg]^{2-}$ or
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CONTINUOUS PROCEDURE FOR THE SIMULTANEOUS COLLECTION
AND PRECIPITATION OF MERCURY IN GASES CONTAINING IT

5 This invention generally relates to a procedure to separate mercury from gases containing it and, more specifically, using a continuous procedure for the simultaneous collection and precipitation in one stage only of the mercury contained within those gases.

10 There are many processes in which gases containing mercury are given off, not only in mercury production factories, but also in other processes such as the obtention of chlorine by the alkaline process, and in calcination, sintering, scrap metal recuperation processes and at plants where sulphured minerals are roasted to fabricate SO_2 and H_2SO_4 , or for the recovery of metals such as lead, copper, zinc, etc.

15 The gases with high mercury content are treated for their purification either dry: decanters, electrostatic precipitators, etc., or wet: washing and cooling, wet electrofilters, etc., but despite these measures the gas, due to the high mercury vapor pressure, may contain significant mercury quantities (a gas cooled down to 30°C may contain up to $30 \text{ mg/m}^3\text{N}$).

20 Both for environmental reasons, if the gases are sent off to the atmosphere, as to prevent contamination of the products manufactured using these gases, it is necessary to effect a thorough purification in order to bring down the mercury content below $0.05 \text{ mg/m}_3\text{N}$.

The state of the art includes the knowledge of a number of methods used to depurate said gases.

30 Thus, German patent 1.075.953 describes the use, to that end, of filters with solid materials, such as coal.

The Spanish patent 451.533 uses the wet method for washing using certain solutions, to which end a two stage process is used, one to collect the mercury through washing in a tower with an aqueous solution of a mercury complex and another stage in which the part of the tower liquid is extracted so as to regenerate oxidizing and precipitating part of the mercury.

Spanish patents 411.067, 556.731 and 9000643 claim a roasting gases purification process in which mercury is oxidized with the SO_2 itself, contained within the gas.

10

Furthermore, patent 9000643 claims that said process is effected in two stages using two irrigation towers with an aqueous solution containing thiocyanates and active coal, with a wet electrofilter between them.

15 The processes of the prior technique described with reference to the Spanish patents number 411.067, 556.731 and 9000643 are applicable only to gases containing SO_2 .

This invention provides now a procedure for the collection and recovery of the mercury contained in combustion gases, roasting gases and other gases containing mercury in gaseous state, through direct precipitation of the mercury in the form of mercuric sulphur.

25 The procedure of the invention has only one stage and takes place in just one tower, consisting of passing the mercury gas through a washing tower where hydrogen sulphur (gas) is injected continuously or intermittently at the same time that it is watered with a solution containing a mercury complex (II) stable in semi acid, such as $[\text{I}_4\text{Hg}]^{2-}$ or $[(\text{SCN})_4\text{Hg}]^{2-}$, without requiring the use of an additional oxidant.

30

Therefore, and in accordance with the above statements, the invention provides a procedure to separate Hg from gases containing it, through contact

with said gases, in a washing tower, with a solution containing a Hg complex (II) stable in semi acid, that may contain active carbon in suspension, characterized because the collection and precipitation of Hg as mercuric sulphur and the regeneration of the Hg (II) complex takes place simultaneously and in only one stage through injection of gaseous SH₂ in said washing tower.

Conveniently the gas temperature at the tower entrance must not be greater than 50°C.

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In accordance with one embodiment of the present invention, a continuous procedure for the simultaneous collection and recovery of mercury from a mercury-containing gas comprises:

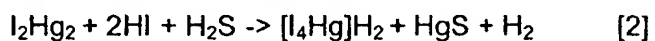
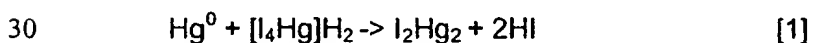
15 passing a mercury-containing gas through a washing tower;

contacting the gas within the tower simultaneously with gaseous hydrogen sulphide and with a solution containing a mercury (II) compound stable in weak acid medium;

20

whereby collection and recovery of the mercury as precipitated mercury (II) sulphide and regeneration of the mercury (II) compound take place simultaneously.

25 Pursuant to the invention, the collection and precipitation of the mercury takes place as per a number of reactions in which mercuric compounds are formed which are immediately oxidized and precipitated as mercuric sulphur (II). These reactions may be summarized as follows.



In case of using thiocyanate as chelating anion, the reactions would be the same substituting the I^- for SCN^- .

5 As may be observed in the reaction above, the concentration of the mercuric complex remains unaltered if the hydrogen sulphur injection is effected in a controlled way, due to which is not necessary to extract the liquid from the tower to regenerate it as the state of the art required up to now.

10 The addition of hydrogen sulphur is easy to control, given that it is sufficient to analyze the solute Hg (II) and maintain it at a previously fixed solution.

15 If iodine anion is used as a chelating agent, the Hg (II) concentration must then be kept between 0.3 and 1.0 g/l, whereas it must be kept between 3 and 10 g/l if thiocyanate anion is used as a chelating agent. It is possible to work with larger Hg (II) concentrations but it is not advisable, both from the financial point of view, given that a greater chelating anion concentration would then be required, as from the practical point of view, given that the purified gas may be contaminated if the washing solution with high mercury content is drawn off.

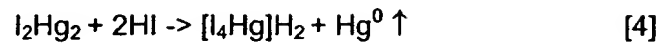
20 The chelating anion concentration must be greater than the stoichiometric quantity to form the mercury complex (II) so as to prevent the intermediate mercuric compounds from becoming stable.

25 The washing solution must be slightly acid and as the acidity is not modified during the process, it is sufficient to add 2 g/l of H_2SO_4 when initially preparing the washing solution.

30 Notwithstanding this, the use of greater acid concentration does not decrease the efficiency of the system.

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In some cases, whenever the gas mercury content is high, the reaction of the dismutation:



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may be faster than the oxidation and precipitation reaction [2]. Active carbon that absorbs the Hg^0 and facilitates its oxidation and precipitation may be used to prevent the Hg^0 being given off.

The procedure of the invention is characterized by its simplicity, given that the whole process takes place in just one stage, using a sole washing tower.

5 In order to illustrate the invention in greater detail, reference is made now to the enclosed drawing, which shows a scheme of execution of the procedure as per the invention.

10 As shown in figure 1, the tower has an inlet for gases containing mercury (1), a H_2S (gas) injector (2), a tank containing the washing solution (3), fitted with a purging outlet (4) to extract solids containing mercury and an inlet (5) through which reactives are introduced. The liquid is impelled using the pump (6) through the pipe (7), fitted with a sampling valve (8), and to the device (9) watering the filling (10). The gas crossing the tower passes through a drop separator (11) and comes out, already purified of mercury, through the conduit (12).

20 The procedure of the invention presents clear advantages over current state of the art processes, among which advantages the following may be emphasized:

- 25 - The process takes place in just one stage and only requires a washing tower. Spanish patent 9000643 claims the use of two watering towers and a wet electrofilter placed between the two towers.
- 30 - It is not necessary for the gases to be purified to contain SO_2 to oxidate elemental mercury, as stated in Spanish patents 411.067, 556.731 and 9000643. Because of this, the invention hereby presented is applicable not only to gases resulting from roasting sulphurated minerals, but also to other type of gases containing mercury.
- 35 - Neither a second stage to regenerate the solution nor the use of an additional oxidizing agent are required, as

claimed in Spanish patent 451.533.

5 The injection of H_2S (gas) in the washing tower itself is the key of the process according to the invention, given that its addition

- Does not modify the watering liquid volume, given that it is injected in a gaseous state.
- 10 - Does not modify the concentration of ions in solution, given that the sulphur precipitates forming mercury sulphur (II) and the hydrogen supplied is compensated by that given off by the oxidation of elemental mercury and acidity does therefore remain constant.
- 15 - Does not modify the concentration of the mercury complex (II) as may be observed in the reaction [3].

20 As a consequence of this, it is not necessary to extract liquid from the tower to regenerate it, as claimed in Spanish patent 451.533. It is only necessary to purge the solids that contain the precipitated mercury and to compensate the mechanical losses of reactivities. The H_2S (gas) is the only product consumed in the reaction and in very small quantities, 0.17 kg of H_2S per kg of purified Hg.

25 Next, the procedure of the invention shall be described with reference to the following examples, which must be considered as merely illustrative in respect of the scope of the invention and under no circumstances must they be interpreted as limiting the invention in any way.

30 Example 1

35 A current of Hg^0 saturated N_2 at $20^\circ C$ (15 mg Hg^0/m^3N) maintaining a 30 l/h flow rate, together with 7 l/h of another N_2 current containing 9 ppm of H_2S was made to flow through a washing vessel containing a solution with 0.5 g/l of Hg (II),

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3 g/l of I^- and 5 g/l of H_2SO_4 . These conditions were maintained over 120 hours, the outlet gas was analyzed and the concentration at all times was lower than 0.05 mg/m^3N .

5 Example 2

10 In a tower as that shown in figure 1 were treated $50.000 \text{ m}^3N/h$ of gas coming from a blende roasting oven containing 7% of SO_2 and a $25 \text{ mg/m}^3 \text{ Hg}^0$ content. The gas entered the tower at a temperature of 30° C . The H_2S injection was 140 l N/h . The washing solution contained 8 g/l of $Hg(II)$, 13 g/l of SCN^- 10 g/l of H_2SO_4 and 2 g/l of active coal. The purified gas at the tower outlet contained $0,03 \text{ mg}$ of Hg^0/m^3N . This gas was used to manufacture sulfuric acid and the mercury content in the acid was lower than 0.5 ppm.

15

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE
PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A continuous procedure for the simultaneous collection and recovery of
5 mercury from a mercury-containing gas, the procedure comprising:

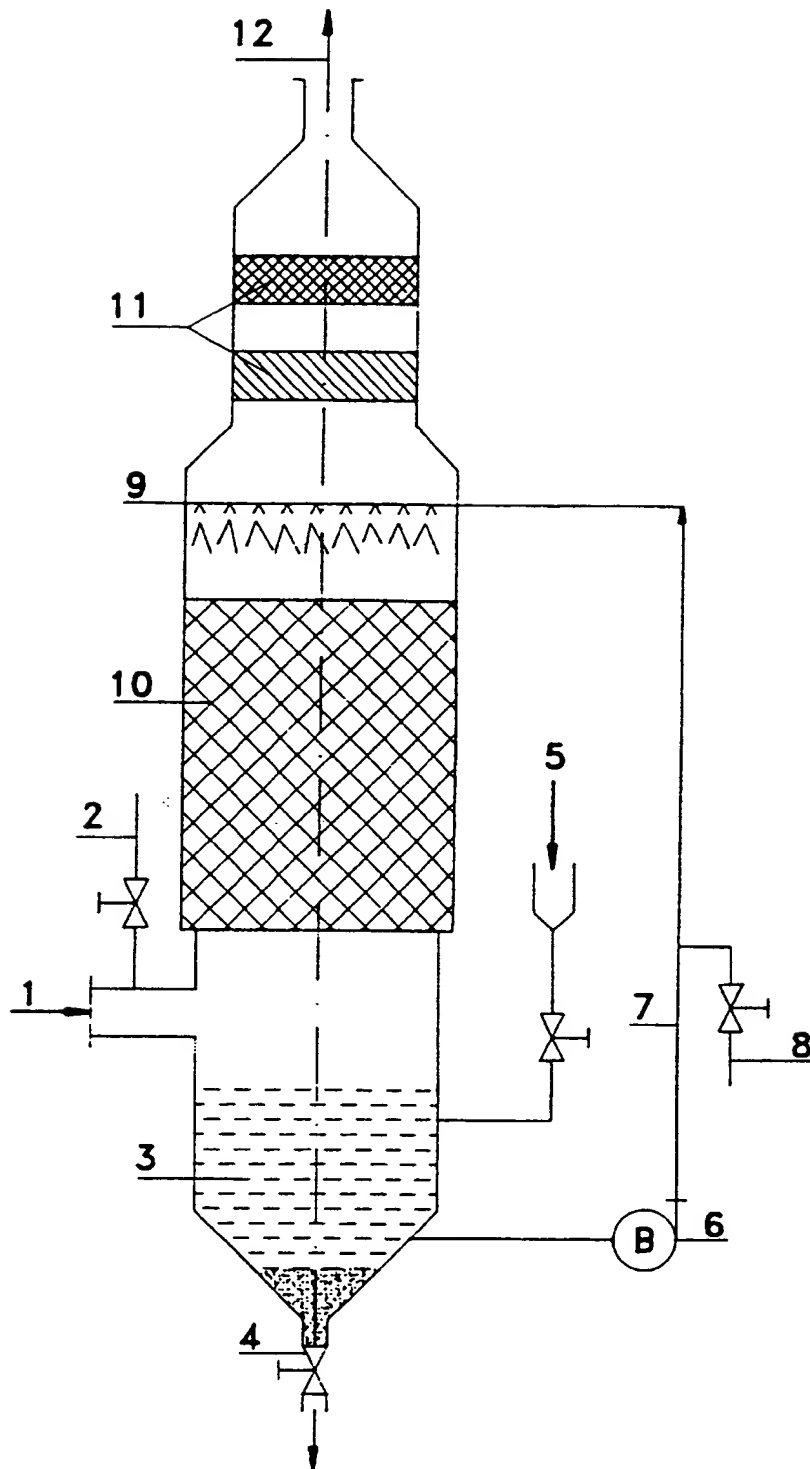
passing a mercury-containing gas through a washing tower;

contacting the gas within the tower simultaneously with gaseous
10 hydrogen sulphide and with a solution containing a mercury (II)
compound stable in weak acid medium;

whereby collection and recovery of the mercury as precipitated
mercury (II) sulphide and regeneration of the mercury (II) compound
15 take place simultaneously.
2. The procedure of claim 1, wherein the solution also contains active
carbon in suspension.
- 20 3. The procedure of claim 1 or 2, wherein the mercury-containing gas is
contacted with an amount of gaseous hydrogen sulphide
stoichiometrically equal to the amount of mercury in the gas.
4. The procedure of claim 1 or 2, wherein the amount of gaseous
25 hydrogen sulphide is regulated based on the analysis of mercury (II) in
the solution.
5. The procedure of claim 1 or 2, wherein the mercury(II) compound is
30 $[(SNC)_4Hg]^{2-}$.
6. The procedure of claim 5, wherein the amount of mercury(II) in solution
is at least 3.0 g/L.

7. The procedure of claim 1 or 2 wherein the mercury(II) compound is $[I_4Hg]^{2-}$.
- 5 8. The procedure of claim 7, wherein the amount of mercury(II) in solution is at least 0.3 g/L.
9. The procedure of claim 5, wherein the concentration of the anion forming the mercury (II) compound is greater than the stoichiometric
10 amount required to form the mercury (II) compound.

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